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## HEAT TREATMENT OF HIGH-TEMPERATURE MERCURIAL THERMOMETERS.

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The ease with which mercurial thermometers can be used, their comparative simplicity and small cost, and the convenience of a direct reading temperature scale have led to the extension of their use to temperatures so high that the ordinary methods and precautions are insufficient. The apparent simplicity of the instrument often seems to hide the real sources of error.

Measurement of temperature, with greater or less accuracy, plays an important part in so many physical and chemical operations, both scientific and industrial, that not every user of a thermometer can be expected to be familiar with the peculiar properties of different kinds of glass and the various changes which may take place in them. If, however, it becomes necessary to determine with any approach to accuracy temperatures higher than about 300° C. (Centigrade degrees will be understood throughout this paper unless otherwise specified), special precautions must be taken, and a knowledge of some of the thermal properties of glass at high temperatures is desirable.

The precision attainable with mercurial thermometers at high temperatures is so largely determined by conditions of use that no definite limits can be assigned, but it may be said that to determine a temperature absolutely to within one degree at 450° requires considerable care. A thermometer may, however, repeat its readings more closely than one degree.

Great changes in indications may arise from continued use at high temperatures, even in thermometers which are properly made. These changes may generally be determined and proper corrections applied unless the glass is unsuitable or the instrument is not well made.

**1. CONSTRUCTION OF HIGH-TEMPERATURE MERCURIAL THERMOMETERS.**

Of the several kinds of glass commonly in use for thermometers, four are suitable for high-grade instruments. These are French hard glass ("verre dur"), Jena 16<sup>III</sup> or "Normal" glass, Jena 59<sup>III</sup> borosilicate thermometer glass, and Greiner and Friedrichs "Resistenzglas." Of these four the first two are not suited for use at temperatures much above 450° (840° F.). The Jena 16<sup>III</sup> glass is more generally used in this country either for the whole thermometer or for the bulb alone with a stem of some other glass. Jena 16<sup>III</sup> glass cracks easily from sudden changes of temperature or even with no apparent cause. This tendency, however, has not been observed in the bulbs. Above 450° it is necessary to use a harder glass. The one most used in this country seems to be the Jena 59<sup>III</sup> borosilicate thermometer glass. The firm of Schott and Genossen, makers of the Jena glasses, has also developed other glasses (notably 122<sup>III</sup>) suitable for high-range thermometers, but which have not yet come into general use. Thermometers are made from the 59<sup>III</sup> borosilicate thermometer glass with scales running up to 550°, but experience has shown that they can not be used at this temperature continuously without undergoing great changes of the "ice point."<sup>1</sup> In fact, it is not safe to go above 530° for any great length of time.

When mercurial thermometers are used at high temperatures, some means must be provided to prevent distillation or boiling of the mercury. Even at 100°, if the top of the mercury column is heated and the tube above it is cool, particles of mercury collect slowly in the cooler parts of the stem. To prevent this below 200° it suffices to keep the top of the mercury column cool or the whole of the stem heated; but if the temperature is much in excess of 200° (390° F.), mercury will begin to boil in a thermometer sealed free from air if the top of the stem is cool. Boiling can be prevented at any temperature by filling the upper part of the stem with gas under sufficient pressure. The pressure required at 400° is about two atmospheres, at 550° twenty atmospheres, and at 750° sixty atmospheres. Two methods are in use for producing the necessary pres-

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<sup>1</sup>The term "ice point" is used to designate the reading on the thermometer immersed in melting ice, in place of the more ambiguous term "zero."

sure. These may for convenience be called the *small* upper bulb and the *large* upper bulb methods. The first is to make a very small bulb at the end of the tube or to leave a portion of the capillary at the end of the scale, and seal off at atmospheric pressure with the mercury standing at some lower point, say  $0^{\circ}$ . Evidently, if the size of the upper bulb is properly chosen the mercury on rising will compress the contained gas, increasing the pressure sufficiently to prevent boiling at all temperatures on the scale. It is not sufficient that the pressure be enough to prevent boiling at the highest points, but it must be determined for intermediate points as well. It might be too low at  $450^{\circ}$  and more than high enough at  $550^{\circ}$ .

The large upper bulb method has some marked advantages, though it is more difficult of application. In this method the end of the stem is provided with an auxiliary bulb or reservoir which is *large* in proportion to the volume of the stem itself, say twenty times the internal volume above zero degrees. This bulb is then filled with some suitable gas under sufficient pressure to prevent boiling of the mercury at the highest points on the scale. To seal off the top under pressure a little shellac or fusible metal is placed in a small tube connecting with the auxiliary bulb and is heated so that it flows down and seals up the small tube while still under pressure. The pressure may then be removed from the outside and the glass tube sealed off beyond the shellac in the ordinary way.

When the *small* upper bulb is used, the internal pressure increases rapidly as the temperature rises, depressing the readings of the thermometer. These variations will not have the same value in different instruments. When the *large* upper bulb is used, the pressure being nearly the same at all parts of the scale, the pressure correction is nearly a constant for any given instrument and does not affect the temperature scale defined by it. For filling the upper bulbs of high-temperature thermometers some inert gas, such as nitrogen or carbon dioxide, should be used free from moisture. If air is present, the mercury soon oxidizes and clings to the walls of the capillary. The use of pure mercury is also important.

The scale of temperature now in almost universal use is that of the hydrogen-gas thermometer, the degree Centigrade being defined as the one one-hundredth part of the change in pressure of a constant volume of hydrogen gas when its temperature is changed

between that of melting pure ice and that of steam from boiling pure water, the initial pressure of the gas at  $0^{\circ}$  being 100 cm of mercury, all under standard conditions. Above  $100^{\circ}$  the degree is similarly defined on the nitrogen-gas thermometer (see Bureau of Standards Circular No. 8). A mercurial thermometer may be graduated to define a temperature scale of its own, dependent only on the properties of mercury and the particular sample of glass. The conditions for such a thermometer are that the degree shall be represented by one one-hundredth of the volume of the stem contained between the readings at the melting point of ice and the steam point of water under standard conditions, and that the scale shall be extended in degrees of the same volume. Such a thermometer made from 59<sup>III</sup> borosilicate glass defines a scale of temperature differing from the scale of the gas thermometer by amounts given below.<sup>2</sup>

TABLE I.

*Variation from the Gas Scale for a Thermometer of Jena 59<sup>III</sup> Glass.*

t	T	t	T
$0^{\circ}$	0	$375^{\circ}$	385.4
$100^{\circ}$	100	$400^{\circ}$	412.3
$200^{\circ}$	200.7	$425^{\circ}$	440.7
$300^{\circ}$	304.1	$450^{\circ}$	469.1
$325^{\circ}$	330.9	$475^{\circ}$	498.0
$350^{\circ}$	358.1	$500^{\circ}$	527.8

where "*t*" represents temperature on the scale of the gas thermometer and "*T*" the corresponding reading on the glass thermometer as defined above. For Jena 16<sup>III</sup> glass thermometers the variation from the gas scale is represented by Table II.<sup>3</sup>

Thus, if a thermometer is intended to read true gas scale temperatures, either the length of a degree must be changed at the higher points, as is generally done in working standards, or proper corrections must be applied. Toward the end of this paper a method is outlined for graduating a thermometer to read gas scale temperature.

<sup>2</sup>Mahlke: *Zs. für Instrumentenkunde*, **15**, p. 178; 1895. Grützmacher: *Zs. für Instrumentenkunde*, **15**, p. 250, 1895.

<sup>3</sup>Wiebe und Böttcher: *Zs. für Instrumentenkunde*, **10**, p. 245; 1890.



TABLE II.

*Variation from the Gas Scale for a Thermometer of Jena 16<sup>111</sup> Glass.*

t	T	t	T
0°	0	240°	240.46
100°	100.00	260°	260.83
150°	149.90	280°	281.33
200°	200.04	300°	301.96
220°	220.21		

## 2. CHANGES IN MERCURIAL THERMOMETERS.

If a thermometer be made with all the above precautions (i. e., proper kind of glass, pure mercury, and sufficient pressure of a neutral gas to prevent boiling) and so calibrated or corrected that it reads true gas scale temperatures at all points, there are a number of changes which will occur in the instrument due to lapse of time and conditions of use. These changes which take place, due to the physical properties of glass, are of two apparently distinct kinds: (1) After a thermometer is newly made there takes place a slow, permanent contraction of the bulb and stem which renders all the readings higher. This contraction is more rapid as the temperature is higher and may even raise the ice point several degrees per hour. (2) All thermometers show changes which are temporary in character. Thus, when a thermometer, after remaining for a long time at room temperature, is heated to 100°, the ice-point reading after this heating will be found *lower* than before, but this "depression" disappears in time if the thermometer is again kept at room temperature. In new thermometers the rise of the ice point may be sufficient to entirely hide this "depression." Thus, there seems to be a position of the ice point corresponding to each temperature. In thermometers of the better glasses, as those mentioned above, this position is reached in a minimum time. In general the time required to reach equilibrium when the temperature is *raised* is very small compared with the time required to reach equilibrium on *lowering* the temperature. For example, if a thermometer of "verre dur," or French hard glass, has been maintained at 0° until its ice point has reached its final position and is then heated to 100°, the position of

the steam point (or in other words the equilibrium condition of the glass) will be reached in ten minutes or less and the reading in ice after this heating will be about  $0^{\circ}.1$  lower than before. But if now the thermometer be kept at  $0^{\circ}$  this depression will not entirely disappear for weeks. This is one reason why all thermometers should be made with the ice point included on the scale, so that these changes may be easily detected. For any of the glasses mentioned above these temporary changes of the ice point are comparatively small. *The depression for  $100^{\circ}$* , i. e., the difference in the ice-point reading taken after a long time at  $0^{\circ}$  and immediately after  $100^{\circ}$ , is as follows:

TABLE III.

*Value of Depression Constant.*

"Verre dur" glass . . . . .	$0^{\circ}.10$ to $0^{\circ}.07$
Jena 59 <sup>III</sup> glass . . . . .	$0^{\circ}.02$
Jena 16 <sup>III</sup> glass . . . . .	$0^{\circ}.07$ to $0^{\circ}.05$

Permanent changes of the first kind are, however, large in all glasses, reaching in some cases a total of  $30^{\circ}$  or  $40^{\circ}$ . They may affect the readings of a thermometer in four different ways: (1) The position of the fixed points of the scale, as the ice point and the steam point, may change. (2) The "fundamental interval" (the number of degrees of the scale comprised between the temperature of melting ice and that of steam from water boiling at normal pressure) may change. (3) The calibration corrections may change, i. e., the volume of the capillary stem per unit length may change by different amounts at different parts of the scale. (4) The temperature scale as defined by the mercury-in-glass thermometer may change relatively to the scale of the gas thermometer. The last two of these effects are so small that it is a question whether they can be determined in ordinary cases. Changes of the fixed points and the fundamental interval, on the other hand, are large, and it is necessary to take account of them.

Change in the fundamental interval may be due either to change in the volume of the capillary or change in the coefficient of expansion of the bulb. Apparently, both of these effects take place simultaneously, for, since the volume of the stem between  $0^{\circ}$  and  $100^{\circ}$  is

about one-sixtieth the volume of the bulb, if we assume that the same changes of volume take place in the stem as in the bulb the variation in the fundamental interval should be about one-sixtieth of the change in the position of the ice point. But, as will be seen from results which follow, the fundamental interval changes from two to three times that amount. For example, if the position of the ice point has changed from  $0^{\circ}$  to  $3^{\circ}$ , the steam point will probably have changed from  $100^{\circ}$  to  $103.1$ . Thus, the fundamental interval has changed from  $100^{\circ}$  to  $100.1$ , i. e., the change has been  $1/30$  that of the ice point and not  $1/60$ , as might be expected.

The position of the ice point can change only on account of a change in the volume of the bulb or of the scale below the ice point. These changes are of far greater magnitude than any of the others, but fortunately they are the most easily determined and allowed for. One object of the present investigation is to determine the nature of the changes in various kinds of glass and to point out methods by which they can be rendered as small as possible.

It has long been known that the position of the ice point of mercurial thermometers may be rendered more permanent by continued heating at high temperatures, and some annealing or artificial aging process is often carried out in their manufacture. In 1837 Despretz<sup>4</sup> made a statement of the general theory as follows: Whenever the molecules of a solid body suffer a displacement from a mechanical cause, as pressure, tension, or torsion, or from a physical cause, such as raising or lowering of temperature, they do not exactly return to their original state when the force is removed—that is to say, if the volume has been diminished or increased more or less by any force whatever it remains diminished or increased for a greater or less length of time after the force has ceased to act. Person<sup>5</sup> was apparently the first to try annealing thermometers, both with and without internal pressure and he carried his temperatures higher than had been previously done. He found that the ice points rose as much as  $17.2$  and suggested prolonged annealing as the remedy for all the defects of glass thermometers. His work,

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<sup>4</sup>Guillaume. *Traité Pratique de la Thermométrie de Précision*, p. 138.

<sup>5</sup>Person *Comptes Rendus*, **19**, p. 1314; 1844.

however, was not carried very far, and he supposed that long annealing would do away with the *temporary* as well as the permanent changes due to heating. Long annealing does not, however, eliminate the temporary changes. Kohlrausch<sup>6</sup> showed that the recovery of the equilibrium condition in glass is much more rapid at higher temperatures. Crafts<sup>7</sup> made a rather extended series of observations on eight thermometers, four of which were of French crystal and four of a lead-free soda glass. His observations extended over a period of about nine months and the conclusions were as follows: (1) Ice points of thermometers of French crystal rise more, and more rapidly, than those of lead-free soda glass. (2) Rise of the ice point is more rapid at first and probably tends toward constancy for a given temperature. (3) An ice point which is raised by long heating remains raised after cooling and the effect of the long heating is to render the ice point more stable for all lower temperatures. The numerical results are of little importance. In another paper this author records some experiments with a large glass balloon showing that at 511° internal pressure does not affect the annealing changes. He here makes application of the above theory of Despertez to explain both the temporary depression and the permanent rise of the ice point thus, when a thermometer is made up before the blowpipe great strains arise in the glass. As the glass cools quickly from the very high temperature used in blowing, the residual strains are large and do not disappear for an indefinite time at ordinary temperatures, but if the temperature is raised these strains begin to be relieved with the result that the bulb contracts, *raising* the ice point. If now this heating be maintained long enough, all the previous strains may have disappeared, but if cooling takes place rapidly from this lower temperature of, say, 400° there will be residual strains corresponding to 400° which will disappear slowly at ordinary temperatures. If all these strains have had sufficient time to disappear, the glass will be free from strains or in equilibrium at ordinary temperatures. Upon heating to, say, 100°, and cooling quickly, it will retain strains corresponding to 100° and the position of the ice point will be *lower* after

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<sup>6</sup>Kohlrausch: Pogg Annal. der Physik, **127**, p. 4, 1866

<sup>7</sup>Crafts: Comptes Rendus, **91**, pp. 291, 370, 413, 1880, **94**, p. 1298, 1882.

heating to  $100^{\circ}$  than it was before. Thus both these apparently opposite variations in the position of the fixed points of a thermometer are referred to the same class of strains in the glass. Crafts also noted changes in the fundamental interval due to annealing.<sup>8</sup>

The work of these experimenters had solved some of the vexed questions in regard to the thermal properties of glass. (1) For every temperature there seemed to be a definite equilibrium condition, which a given sample of glass tends to assume more or less rapidly, depending upon the temperature, the previous history of the sample, and its chemical composition. (2) In general the equilibrium condition follows much more rapidly a rising than a falling temperature, but it takes place more quickly when the temperature is higher. (3) Long heating at higher temperatures renders the ice point more constant at lower temperatures. (4) The coefficient of expansion of glass is affected by its state of internal strains, being less by as much as 3 per cent for glass which is nearly free from strains than for glass which has been rapidly cooled. (5) Equilibrium conditions corresponding to small changes of temperature may occur without materially affecting the slow assumption of the equilibrium condition after more marked temperature changes.

With the above conclusions as a working basis a number of experiments have been carried out by different observers to gain a better knowledge of the peculiarities of different kinds of glass, to determine the magnitude of the changes in different samples and particularly to determine what kinds of glass best meet the requirements of the thermometer manufacturer; and a number of special thermometer glasses have been developed.

In 1883 Weber<sup>9</sup> published the results of an investigation of the effect of chemical composition on the depression constant. He concluded that the chemical composition had a marked effect on the depression constant,<sup>10</sup> that the softer kinds of glass were unsuitable for thermometers, and that the best results were obtained with a pure potassium glass containing large percentages of silicon and calcium. Wiebe<sup>11</sup> (1886) showed that the depression constant is greatest when

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<sup>8</sup> See also Pernet: *Comptes Rendus*, **91**, p. 471; 1880.

<sup>9</sup> Ber. K. Akad. der Wissenschaften, **13**, p. 1233; 1883.

<sup>10</sup> See Table III.

<sup>11</sup> *Zs. für Instrumentenkunde*, **6**, p. 167; 1886, or "Jenaer Glas" by H. Hovestadt.

equal percentages of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  are present in the glass; that it is nearly the same, regardless of which is present in the greater quantity, provided the ratio of one to the other is numerically the same, and that it is least when  $\text{K}_2\text{O}$  only is present. The other constituents seem to have only a small effect on the depression constant.

Another series of experiments by Wiebe<sup>12</sup> on a number of thermometers of different kinds of glass led to the same general conclusions as those quoted above from Crafts. He also found that the glasses which show the smaller depression constant show the smaller rise of the ice point on heating. In a later paper he gives the results of some further experiments on five Jena 16<sup>III</sup> glass thermometers. On heating to 500° these thermometers showed a marked permanent depression of the ice point due to enlargement of the bulbs under internal pressure, as the glass softens at that temperature.

Schott (1891)<sup>13</sup> made an investigation to determine the temperatures at which different kinds of glass begin to soften. His observations were made on short pieces of rod ground plane at the ends and observed between crossed nicol prisms, the number of diffraction bands indicating the condition of strain. These samples had been first rapidly cooled, so that the strains were large. The temperature at which the Jena 16<sup>III</sup> glass began to show unmistakable signs of softening was 400° and that at which the 59<sup>III</sup> glass showed softening was 430°, although these glasses can be used for thermometers with from four to twenty atmospheres internal pressure at 450° and 530°, respectively, without showing any increase in the volume of the bulb. This author describes a method of rendering the strains in the glass visible. A rod of glass is surrounded by a liquid of the same index of refraction in a vessel with plate-glass sides. By examining this rod in polarized light the condition of strain is indicated by the number of diffraction bands which appear. A sample of Jena 59<sup>III</sup> glass which showed innumerable bands before heating, after four days at 445° showed only four. The author shows also that slow cooling of a thermometer renders its subsequent changes smaller.

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<sup>12</sup> Wiebe: *Zs. für Instrumentenkunde*, 8, p. 373; 1898; also 10, p. 207, 1890.

<sup>13</sup> Schott: *Zs. für Instrumentenkunde*, 11, p. 330, 1891.

In Winkelmann's *Handbuch der Physik* (Vol. II., pp. 29-33, 62), there is given a résumé of some of the important work done on the thermal properties of glass, and "Jenaer Glas," by Hovestadt, gives a rather complete outline of most of the experimental work on the subject.

### 3. OUTLINE OF THE PRESENT INVESTIGATION.

Although considerable work has been done on the thermal properties of glass and valuable conclusions have been reached, most of the data obtainable are contained in scattered papers, few of them in English. The demand for information on this subject from a practical point of view as well as the hope of answering more fully some questions regarding the behavior of glass at high temperatures led to the present investigation. Some of the questions for which more definite answers are desirable are as follows:

- (a) How rapidly does the ice point rise at different temperatures?
- (b) How does this rate of rise change with time?
- (c) What is the effect of slow and of rapid cooling?
- (d) What is the effect of short periods of heating?
- (e) What process of heating will render the ice point sufficiently constant for different kinds of glass?
- (f) Can the annealing temperature be lower if the thermometer is to be used only at moderate heat?
- (g) What relation exists between changes in the fundamental interval and those of the ice point?
- (h) Does the use of a different kind of glass, having inferior thermal properties, for the stem of a thermometer introduce any significant errors?
- (i) Does the absence of pressure and mercury from the bulb of a thermometer during annealing affect its changes of volume?

The length of time covered by some of the following series of observations is far greater than in previous investigations.

### 4. APPARATUS.

Fifteen special thermometers (Fig. 1) were obtained in three different sets. The first set consists of four thermometers, three entirely of Jena 16<sup>III</sup> glass and the fourth having a bulb of this glass joined to a stem of ordinary soft glass. The numbers of

these thermometers are as follows: G. 3689, 3690, 3691, and 3692. During the various operations all these except G. 3692, which has a soft glass stem, developed surface cracks and finally broke. The scales of all these thermometers consist of a portion of some  $30^{\circ}$ ,  $10^{\circ}$  below and  $20^{\circ}$  above the  $0^{\circ}$  point, and the same at the  $100^{\circ}$  point separated by an auxiliary reservoir. Also, about the same length of scale is provided at the  $200^{\circ}$  point, with a continuous scale from  $300^{\circ}$  to  $460^{\circ}$  divided into single degrees. The second set of seven thermometers, Nos. G. 4279, 4280, 4281, 4282, 4290, 4291, and 4292, by the same maker, graduated in half degrees, consists of four having bulbs at the top large enough to contain all the mercury and having a scale covering about  $30^{\circ}$  above the  $0^{\circ}$  and above the  $100^{\circ}$  points, and three thermometers with scales running from  $0^{\circ}$  to  $35^{\circ}$ , from  $100^{\circ}$  to  $135^{\circ}$ , and from  $400^{\circ}$  to  $470^{\circ}$ . Two of the former and

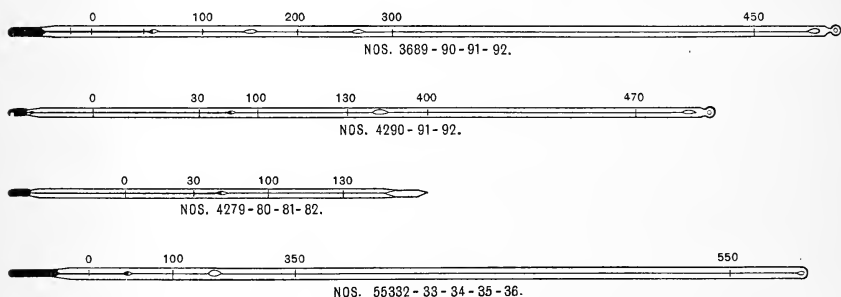


Fig. 1.—*Experimental Thermometers.*

one of the latter have soft glass stems. The other four are of Jena 16<sup>III</sup> glass throughout. The third set consists of four thermometers of Jena 59<sup>III</sup> glass, graduated in single degrees and having scales covering a few degrees at  $0^{\circ}$ , at  $100^{\circ}$ , and a continuous scale from  $350^{\circ}$  to  $550^{\circ}$ . In addition to the four thermometers of this set, the makers kindly loaned us two others of the same construction to be subjected to the same treatment. These six are numbered T. 55332, 55333, 55334, 55335, 55336, and 55337. In regard to all these instruments it was specifically required that the maker should not subject them to any process of aging, but where it was necessary to point the scale at higher temperatures some heating apparently was resorted to. The results of the experiments clearly show the effect of this heating.



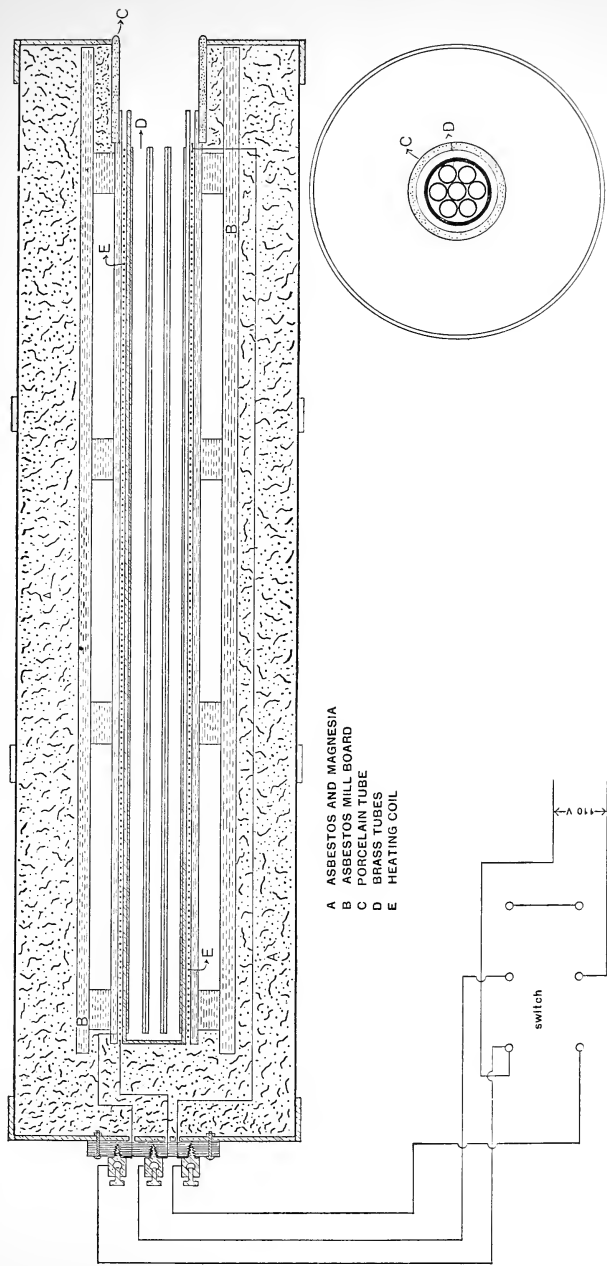


Fig. 2.—Annealing Oven, Showing Section and End View.

It was necessary to provide some means for maintaining high temperatures with fair constancy for long periods of time without undue attention. The annealing oven, which has been used for all the experiments of long duration and which is shown in Fig. 2, was built in the instrument shop of the Bureau of Standards and is of a simple form. A brass tube about 3 cm in diameter was selected to contain seven smaller tubes each large enough to hold a single thermometer. The larger tube was covered with a double layer of thin mica and wound with a *double spiral* of "Advance" resistance wire, No. 24 B. & S. The total number of turns of wire is 240, having a total resistance of about 60 ohms. With this arrangement three different heating combinations are possible. The two coils joined in series give a resistance of 60 ohms, either coil alone a resistance of 30 ohms, or the two in parallel a resistance of 15 ohms. It has been found that sufficient heat is produced with the coils connected in series directly to the lighting circuit of 120 volts to maintain the highest temperatures used, i. e., 550°. The other arrangements are made use of only when it is desired to raise the temperature rapidly. Care was taken to adjust the winding so that the temperature should be as nearly uniform as possible throughout the length of the oven. The brass tubes are about 60 cm long and are surrounded with a packing of magnesia and asbestos in a Russia iron cylinder about 16 cm in diameter and 75 cm long. With reasonable constancy of the lighting circuit the changes of temperature are only 10° or 15° at the most. About 100 watts will maintain 400° in this oven as it is arranged. A rheostat of 80 ohms resistance in steps of 10 ohms each is used in connection with a 10-ohm adjustable dial rheostat. In this way any desired temperature from 150° to 550° may be maintained. The accompanying cut (Fig. 2) shows a double-pole, double-throw switch connected up so as to throw the two portions of the heating coil in parallel or in series at will.

#### 5. OBSERVATIONS.

The procedure in all the observations was to determine the readings of the thermometers in ice, then place those to be tested in the annealing oven, noting the time and temperature. After the desired length of time they were removed from the oven and the readings in ice taken as quickly as possible, except in cases where it was

desired to have cooling take place slowly. In these cases the oven was allowed to cool down by gradually diminishing the heating current until it reached nearly room temperature. Steam point readings were taken from time to time and the values of the fundamental interval computed. It should be noted that as the thermometers are divided only in degrees and half degrees the readings recorded in the tables are not to be depended upon nearer than about  $0.03$  or  $0.04$ . For this same reason the fundamental interval determinations are of only small value, since the changes which take place are often of the order of a few hundredths of a degree.

It could hardly be expected that a series of independent ice point and steam point determinations as long as the present one should not contain some errors. From the very nature of the tests no check could be had upon observations which had once been taken, and there appear a few points on the annealing curves which indicate that some error might have been made. In general, all observations were repeated two or three times at each point, but sometimes small bubbles of gas collect within the bulb of a thermometer which has been heated for a long time and these, if overlooked, introduce errors which no number of readings will reveal. In the case of the four thermometers made with large upper bulbs it was necessary to manipulate the mercury back into the lower bulb for each observation of the ice point, and it was difficult to tell when the last trace of gas had been worked out of the way.

The following table gives the observations taken on one set of the thermometers. In the column headed "Date" is given the time of the corresponding ice point or steam point determination. The column marked "Time" gives the number of hours or days during which the thermometers had been heated since the preceding observation. In the column headed "Remarks" are given briefly the conditions of the annealing, such as temperature of the oven, etc. For example, under series 1, the fifth line indicates that, after heating for 16 hour (or ten minutes) at a temperature of  $200^{\circ}$  the ice point of thermometer No. 3689 read  $-9.72$  and the ice point of No. 3690 read  $-9.73$ , observations being taken on October 24, 1904. Where boiling points are given they are reduced to standard conditions, i. e., what the readings would have been if the barometric pressure had been normal, making the temperature of the steam  $100^{\circ}$ .

TABLE IV.

Observations Taken on Four Jena 16<sup>mm</sup> Glass Thermometers of Series I.

Date	368g	369o	369r	3692	Time	Remarks
1904						
Oct. 24	— 9.76	— 9.72	— 9.67	— 9.99	.....	Zeros before heating.
24	90.03	89.97	90.03	89.78	.....	Boiling point after 10 min.
24	— 9.79	— 9.75	— 9.71	— 10.02	.....	Zeros after boiling point.
24	99.82	99.72	99.74	99.80	.....	Fundamental intervals.
24	— 9.72	— 9.73	.....	.....	1/6 hr	At 200°.
24	— 9.66	— 9.65	.....	.....	1/6 hr	At 250°.
24	— 9.55	— 9.51	.....	.....	1/6 hr	At 300°.
24	.....	.....	.....	— 10.00	2/3 hr	At 100°.
25	— 9.52	— 9.53	.....	.....	19 hrs	At room temperatures.
25	— 9.32	.....	.....	.....	1/6 hr	At 325°.
25	Broke.	— 9.26	.....	.....	1/6 hr	At 350° (3689 repaired).
25	.....	— 5.03	.....	.....	1/6 hr	At 450° Hg. boiled (?).
25	.....	.....	— 9.72	.....	1 hr	At 250°.
26	.....	.....	— 8.55	— 9.17	5 hrs	At 320°.
26	.....	.....	— 8.65	.....	1/4 hr	At from 300° to 400°.
26	.....	99.72	.....	.....	.....	Fundamental interval.
26	.....	— 5.73	— 8.57	— 9.14	20 hrs	At room temperature.
27	.....	94.10	91.20	90.84	48 hrs	Boiling point after rest.
31	.....	— 5.79	— 8.58	— 9.16	1/3 hr	After boiling point.
31	.....	99.89	99.78	100.00	.....	Fundamental interval.
31	.....	— 3.27	— 5.72	— 6.58	22 hrs	At from 335° to 350°.
Nov. 1	.....	96.69	94.32	93.58	.....	Boiling point.
1	.....	99.95	100.05	100.15	.....	Fundamental interval.
1	.....	— 3.26	— 5.73	— 6.57	.....	After boiling for F. I.
2	.....	.....	.....	— 4.68	24 hrs	At from 340° to 360°.
3	.....	.....	.....	— 3.04	23 hrs	At from 350° to 360°.
3	.....	.....	.....	97.18	.....	Boiling point.
3	.....	.....	.....	— 3.03	.....	After boiling point.
3	.....	.....	.....	100.21	.....	Fundamental interval.
4	.....	.....	.....	— 1.27	24 hrs	At 360°.
5	.....	.....	.....	— .48	24 hrs	At 360°.
7	.....	— 3.26	— 5.67	— .47	48 hrs	At room temperature.
10	.....	.....	.....	.07	72 hrs	At 340°.
14	.....	— 3.23	— 5.69	.....	14 days	At room temperature.
14	.....	.....	.....	.38	.....	Slowly cooled 36 h. Heated to 300°, 5 min.
15	— .93	.....	.....	.....	.....	First observation since repairing.
21	.....	— 3.35	.....	.27	1 hr	At 254°.
22	.....	— 3.42	.....	.18	1 hr	At 295°.
23	.77	.....	.....	.....	22 1/2 hrs	At 297°.
25	.....	— 3.35	.....	.15	48 hrs	At room temperature.
25	.....	— 3.28	.....	.00	1 hr	At 340°.
26	25.1	.....	.....	.....	23 hrs	At 445° and slowly cooled.
29	.....	— 3.17	.....	.11	1 hr	At 320°.
30	.....	— 3.39	.....	.....	1 hr	At 367°.
Dec. 5	.....	— 3.16	.....	.....	1 hr	At 375° on Dec. 1.
5	.....	.....	— 5.64	.....	35 days	At room temperature.
1905						
Feb. 6	24.97	— 3.18	— 5.66	.18	.....	At rest since last recorded observations.
15	.....	.....	.....	8.46	21 hrs	At 450°.
17	.....	.....	.....	11.23	21 hrs	At 450°.
Mar. 14	.....	.....	.....	11.31	2 min	At 500°.
15	.....	.....	.....	12.93	18 hrs	At 435°.
15	.....	.....	.....	111.47	.....	Boiling point.
15	.....	.....	.....	12.93	.....	After boiling point.
15	.....	.....	.....	(98.54)?	.....	Fundamental interval.
18	.....	.....	.....	13.18	.....	Continuous use up to 400°.
18	.....	— 3.17	— 5.58	.....	.....	At rest since last recorded observations.
May 1	.....	.....	.....	13.48	.....	In general use.
18	.....	.....	.....	13.26	1/2 hr	At 360°.
Aug. 22	.....	.....	.....	13.38	.....	In general use since May 24.

The accompanying curves (Figs. 3, 4, 5, 6, 7) give in graphic form the results of practically all the observations made on the ice points of the seventeen thermometers included in the experiments. The variations which take place during the first few hours are very much larger and more rapid than any which follow, unless the temperature be later increased. In order to show more clearly these early changes the first few hours are plotted on a much more open scale, so that Figs. 4 and 7 cover ten times the length of time of Fig. 3 and Fig. 6, respectively, and Fig. 5 covers five times the number of hours on Fig. 4 or fifty times the number on Fig. 3. For example, if the curves representing all the experiments in series No. 1 were plotted on the same scale as Fig. 3, their length would be about 25 meters. The ice-point readings are represented as ordinates and the number of hours annealing previous to the ice-point determination as abscissas. Since the position of the ice point is a complex function not only of the time, but also of the temperature, of annealing, and since it was desired to learn as much as possible of the nature of this complex function the temperatures were not in general maintained constant. The temperature of the annealing oven is therefore entered on each section of the curves, representing what should properly be a third dimension. For an example of the meaning of the curves it may be noted that the curve marked "G. 4281," beginning with Fig. 3 of series No. 1, should be interpreted as follows: Thermometer No. 4281 at the beginning of the experiments had a reading of  $-0^{\circ}.1$  observed in melting ice; after heating for about 20 minutes at  $100^{\circ}$  (or in steam) the observed reading in ice was  $-0^{\circ}.14$ ; then after 2 hours 20 minutes heating at a temperature of  $380^{\circ}$  the ice point was  $4^{\circ}.58$ ; after 1 hour 40 minutes the ice point was  $5^{\circ}.24$ , and so on. In Fig. 6 of series No. 2 the curve marked "T. 55336" indicates that during a heating of about 53 hours at a temperature of  $528^{\circ}$  the position of the ice point had fallen from  $9^{\circ}.0$  to  $-34^{\circ}.0$ . This marked lowering of the ice-point reading is due to actual enlargement of the bulb of the thermometer from internal pressure and softening of the glass; hence, this temperature is too high to measure with this instrument. Series No. 1 gives the results of experiments on thermometers of Jena 16<sup>m</sup> glass and series No. 2 on those of Jena 59<sup>m</sup> glass.



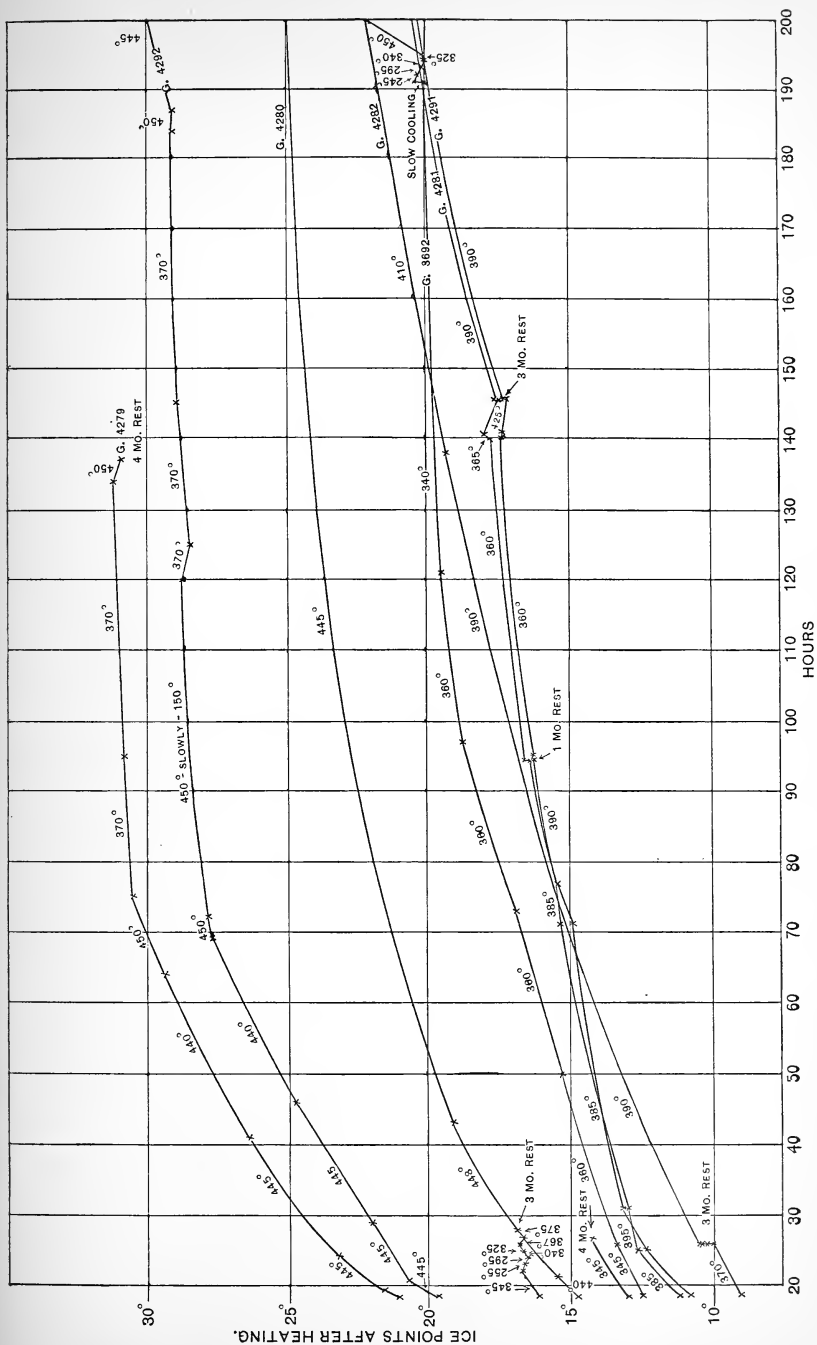


Fig. 4.—(Series 1—Continued.)  
Ice-point changes due to continued heating up to 200 hours at temperatures indicated on the curves.  
Thermometers of Jena 16<sup>III</sup>, "normal" thermometer glass.

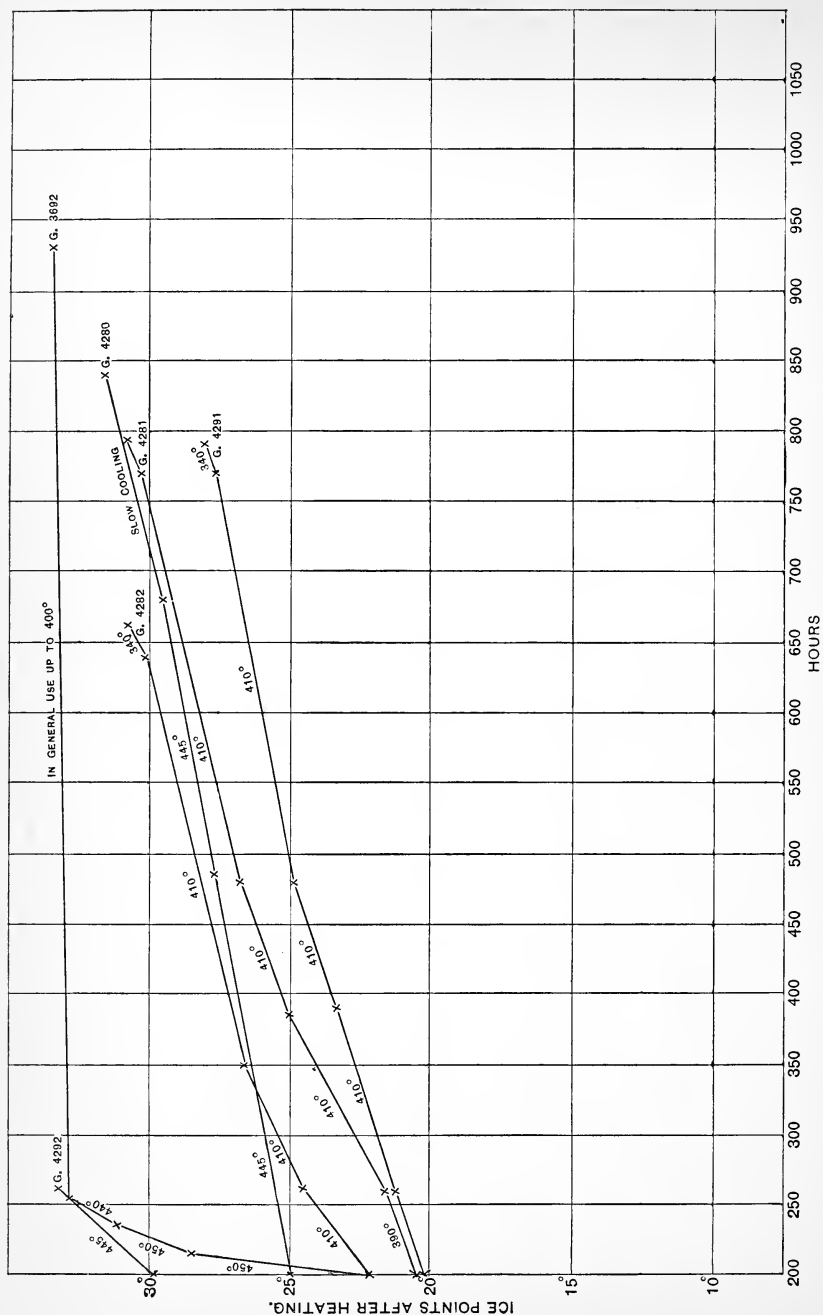


Fig. 5.—(Series 1—Concluded.)

*Ice-point changes due to continued heating up to 1,000 hours at temperatures indicated on the curves. Thermometers of Jena 16<sup>III</sup>, "normal" thermometer glass.*



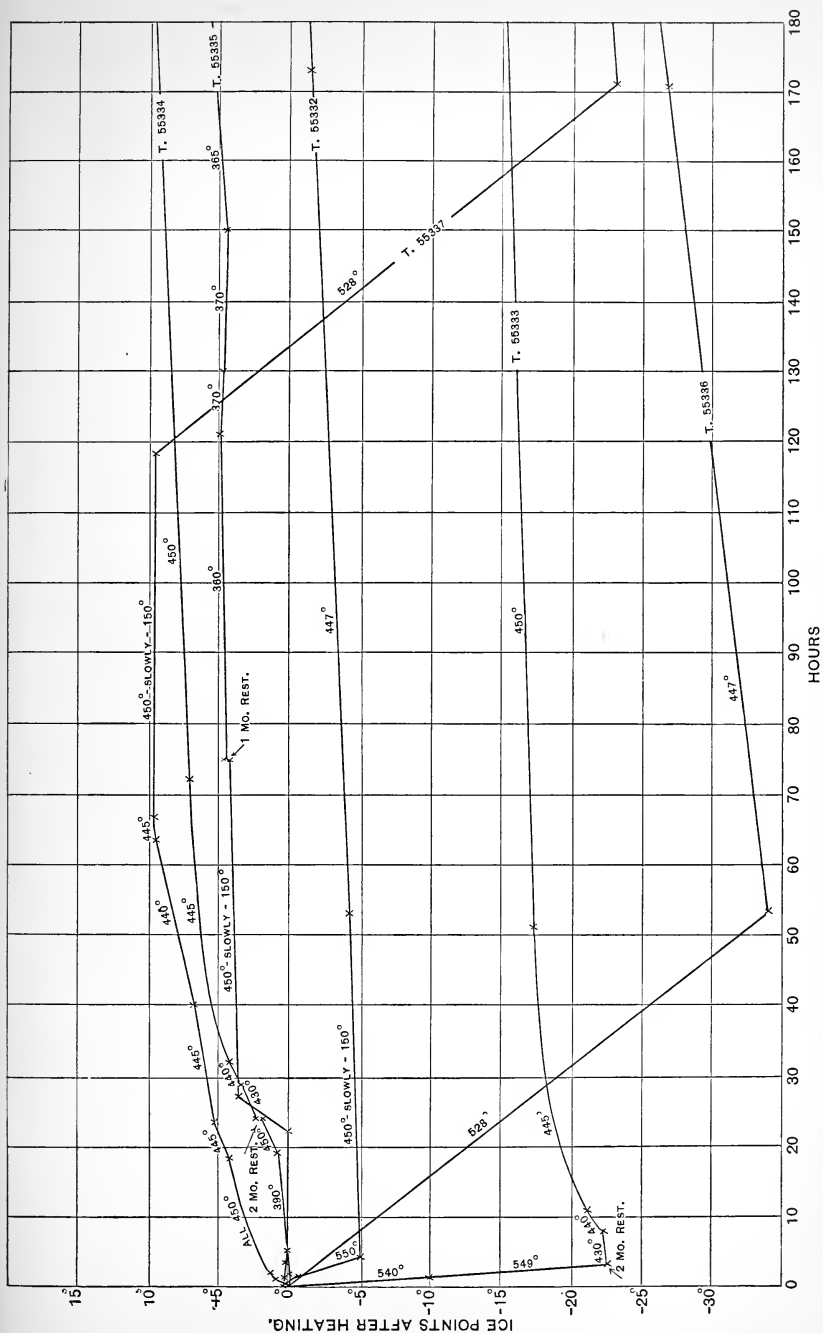


Fig. 6.—(Series 2.)  
Ice-point changes due to continued heating up to 180 hours at temperatures indicated on the curves.  
Thermometers of Jena 59<sup>III</sup>, borosilicate thermometer glass.

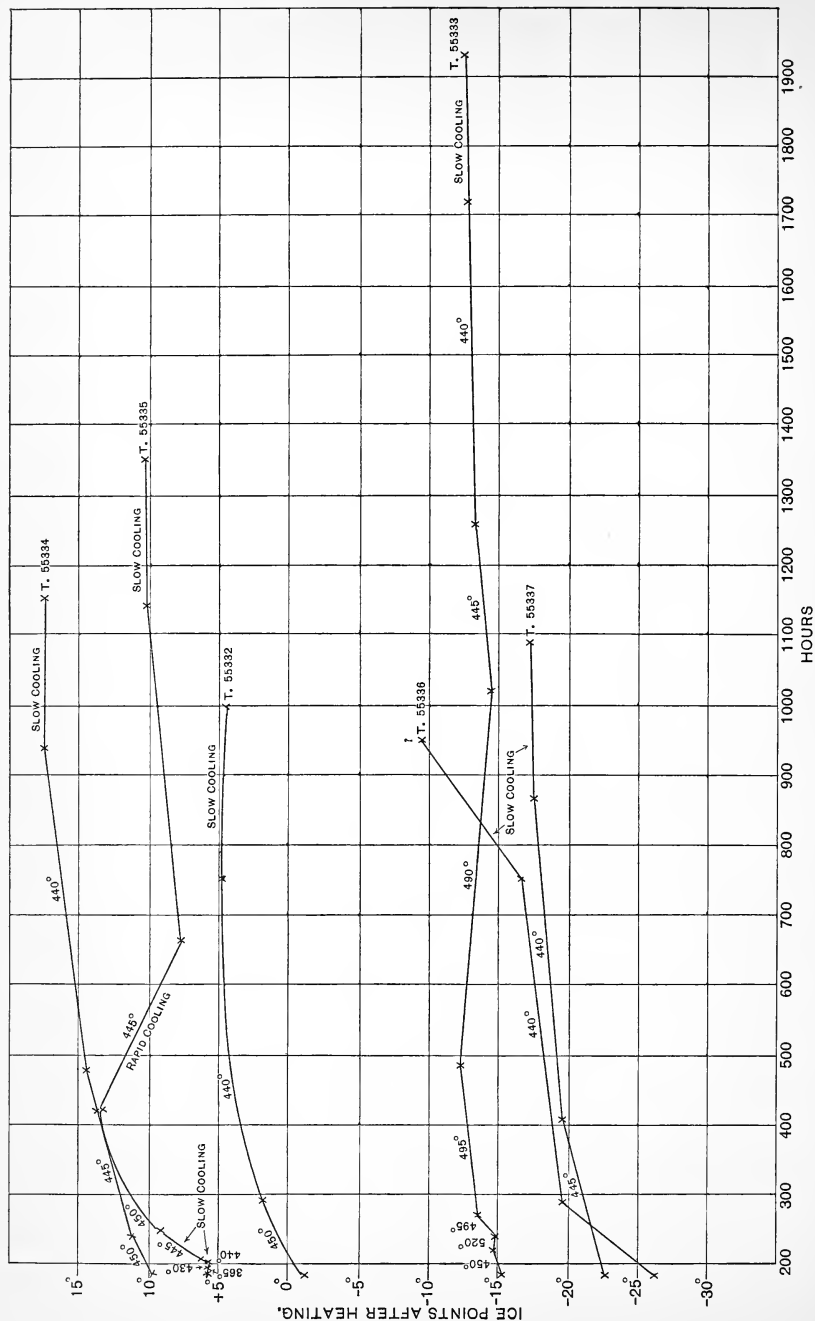


Fig. 7.—(Series 2—Concluded.)  
Ice-point changes due to continued heating up to 2,000 hours at temperatures indicated on the curves.  
Thermometers of Jena 59<sup>m</sup>, borosilicate thermometer glass.

## 6. DISCUSSION OF RESULTS.

The results of the present experiments have been put in graphic form with the belief that in that way they could be most readily studied. The conclusions stated hereafter are founded on the results of previous investigations as well as those embodied in accompanying tables and curves, the examination of which leads to answers to some of the questions previously suggested.

(a) A newly filled thermometer which has not been subjected to heat, when first subjected to temperatures higher than that of the room will show a change of its ice point which may be in either direction and of varying magnitudes, depending upon the temperature, the nature of the glass, the length of time heated, and the previous treatment. If the temperature be not more than  $100^{\circ}$  or  $150^{\circ}$  and the heating continue only for some minutes the ice point reading will be lowered by a small amount (e. g.,  $0^{\circ}.1$  or  $0^{\circ}.2$  for Jena "normal" glass). If the temperature be higher than about  $150^{\circ}$  for Jena "normal" glass or  $400^{\circ}$  for the borosilicate glass, or in any case if the time be long enough, the ice point reading will *rise*. This rise will be much more rapid at higher temperatures, the changes during the first hour being roughly as follows :

TABLE V.

*Rise of the Ice Point during First Hour's Heating at Different Temperatures.*

Jena 16 <sup>III</sup> Glass		Jena 59 <sup>III</sup> Glass	
Temperature	Ice Point Rise	Temperature	Ice Point Rise
200°	0°1	300°	—0°1 (drop)
300°	0°3	400°	—0°1 (drop)
350°	0°7	450°	+0°7
400°	2°5		
450°	8°0	550° shows a decided drop.	

Thus the change of ice point during the first hour's heating of a Jena 16<sup>III</sup> glass thermometer at  $450^{\circ}$  is of the order of ten times that for the same time at  $350^{\circ}$ . About the same proportion would probably apply for 59<sup>III</sup> glass between  $425^{\circ}$  and  $525^{\circ}$ . In the present series of experiments all the thermometers of this glass

showed a decided lowering of the ice point when heated much above  $500^{\circ}$ . Results obtained from the instruments after this lowering had taken place, due to internal pressure and softening of the glass, would obviously be uncertain.

The observations indicate that a certain amount of annealing took place at the same time that the bulbs were being enlarged by overheating, since the subsequent heatings changed the ice point less than if the thermometers had not been overheated. This effect may be seen by comparing the curves for T. 55333 and T. 55334 in series 2. The former had its ice point depressed by  $22.5^{\circ}$  and in the course of 500 hours heating afterwards the ice point rose by about  $10^{\circ}$ , while the latter, which did not suffer such a lowering, shows a rise of about  $15^{\circ}$  in the same length of time and under less severe conditions of heating.

(b) The change of ice point is much more rapid during the first few hours, and becomes slower as time goes on; but apparently the time required to reach a limiting position is very long. Some of the thermometers have been observed after heating for a total of over 1,900 hours (80 days), and still show slow changes. The rates at which ice points change are shown approximately by the following table:

TABLE VI.

*Rise per Hour of the Ice Point after Different Lengths of Time at Various Temperatures.*

Jena 16 <sup>III</sup> Glass			Jena 59 <sup>III</sup> Glass		
Temperature	Time	Rise per Hour	Temperature	Time	Rise per Hour
350°	50 hours	0°1	400°	50 hours	0°02
400°	50 "	.07	450°	50 "	.02
450°	50 "	.05	500°	50 "	(.02)
350°	200 "	.01	400°	200 "	No data
400°	200 "	.006	450°	200 "	.01
450°	200 "	.003	500°	200 "	.008
			500°	500 "	.00 ?

This table shows that the change of the ice point is very slow after 200 hours' annealing, and for 59<sup>III</sup> glass is almost inappreciable after 500 hours' heating at  $500^{\circ}$ .

(c) For temperatures a few degrees lower than that at which the annealing has taken place the changes are very small even after one hundred hours, but if the thermometer has been quickly cooled it will show a sudden small rise of the ice point on heating up to a temperature a little lower than that from which it was cooled. This effect is small but has been repeatedly observed even after a long time has elapsed. These observations after long rest indicate that the strains remaining after rapid cooling from, say,  $400^{\circ}$  or  $500^{\circ}$  do not disappear to any large extent at room temperature. For this reason it is best that a thermometer should be slowly cooled after annealing. If cooled slowly the glass has time to take up its equilibrium condition at each stage of the temperature drop. For example, when a sample of glass has been kept for a long time at  $450^{\circ}$  it will be nearly free from strains at this temperature, but on cooling strains are introduced. If quickly cooled to room temperature these strains will persist for a very long time, perhaps for years, but the strains left from heating at  $450^{\circ}$  will nearly all disappear at  $430^{\circ}$  in a few hours, and again the strains left from heating to  $430^{\circ}$  will soon disappear at  $400^{\circ}$ , and so on. At  $25^{\circ}$  the strains due to cooling from a temperature of  $100^{\circ}$  will be inappreciable after a few days. Thus it is possible to have the glass of a thermometer almost entirely free from strains at a temperature of  $25^{\circ}$  by this process, whereas if cooled rapidly this condition would not be reached in a very long time, perhaps not in years.

(d) If a number of similar unannealed thermometers originally reading alike at the ice point be subjected to different short periods of heating the ice-point readings will be very different. And if now these thermometers be put together in an annealing oven at a temperature higher than that to which they have been previously subjected, a few hours will suffice to make them all read nearly alike. Hence it seems that short periods of annealing at lower temperatures have no marked effect on the total time subsequently required to satisfactorily anneal a thermometer at a higher temperature; e. g., it would take as long at  $400^{\circ}$  to bring the ice-point reading up to  $+25^{\circ}$ , whether starting with a thermometer which had previously had its ice point raised to  $15^{\circ}$  or with one not previously heated, provided both read  $0^{\circ}$  in ice when newly made. Thermometers G. 4279 and G. 4292 or G. 4281 and G. 4291 (see Fig. 3), though they differed

by more than  $4^{\circ}$  at the start, came to the same ice-point reading after the first few hours' heating. The difference in the initial positions of the ice points is presumably due to the treatment by the maker in pointing G. 4291 and G. 4292 at the higher parts of the scale; G. 4279 and G. 4281 not being pointed above  $100^{\circ}$  were not thus affected. The same effect may be seen by comparing G. 3692 with G. 4279 and G. 4281. Though the first was annealed for many hours at a lower temperature, the time required to reach a given rate of rise at  $445^{\circ}$  was almost identical in all three cases. The previous history and original ice point of G. 3692 are not known, but it had probably not been heated above  $445^{\circ}$ . It seems to make little difference in the final results whether annealing takes place with continuous heating or in short periods of the same total length.

(e) As previously noted Schott has shown that total disappearance of the residual strains is possible at from  $400^{\circ}$  to  $410^{\circ}$  for Jena 16<sup>III</sup> glass and  $430^{\circ}$  to  $440^{\circ}$  for Jena 59<sup>III</sup> glass. The results of the present investigation seem in general to confirm this conclusion. Thermometers G. 4281, G. 4282, and G. 4291 after long annealing at about  $410^{\circ}$  seem to have reached the same condition as G. 4279 and G. 4292, which have been annealed at about  $450^{\circ}$ . From the observations on thermometers annealed at from  $300^{\circ}$  to  $350^{\circ}$  it appears that the time required at these temperatures to reach complete annealing or freedom from strains, which apparently would mean a rise of the ice point of about  $30^{\circ}$ , is excessively long if such a condition would ever be attained. There are no conclusive examples in the case of the Jena 59<sup>III</sup> glass. In this case if the thermometers are to be used up to  $500^{\circ}$  it would probably be better to make the annealing temperature higher to save time, though a long enough period at  $450^{\circ}$  might accomplish the same result. In respect to length of time required, the present observations do not appear to agree with Schott's conclusions reached by his optical method. The time required to attain anything like constancy of the ice point has been found much longer than the four days which he found sufficient to relieve practically all the strains he could observe. It is possible that the residual strains which he observed, and which are referred to in the earlier part of this paper, were of greater importance than appeared, but it is not clear that one is justified in assuming that all the strains which give rise to changes

in the volume of glass as indicated by changes of the ice point are of such a nature that they can affect its optical properties as observed with polarized light.

(f) When a thermometer has been annealed for a short time at some high temperature, as, say,  $450^{\circ}$ , and is then kept at some lower temperature, the rate of rise of the ice point is much slower on account of this heating. Thus, a relatively short annealing renders the ice point much more stable for lower temperatures. This fact may be explained thus: For example, the total rise of the ice point during fifty hours' heating at  $400^{\circ}$  is  $15^{\circ}$  and the rate of rise after such heating is  $0.05^{\circ}$  per hour. Then if the thermometer were annealed at  $450^{\circ}$  (instead of  $400^{\circ}$ ) for about seven hours the total rise of the ice point would be about the same ( $15^{\circ}$ ) and the rate of rise at  $400^{\circ}$  after this treatment would probably be about the same as if the annealing had been done at  $400^{\circ}$ , and had continued for fifty hours. In other words, the rate of change per hour at a given temperature, as  $400^{\circ}$ , will be nearly the same for thermometers of a given kind of glass when the ice point has been raised to any given extent, as, say,  $15^{\circ}$ , independently of whether that rise of the ice point has been produced by heating for a *short* time at a *high* temperature or for a *longer* time at a *lower* temperature. Thus if a thermometer is not to be used at the highest temperatures the time of annealing may be diminished or the temperature of annealing may be lower.

(g) The steam point and fundamental interval have been determined several times for each thermometer, but owing to the fact that the instruments are only divided to degrees or half degrees these determinations can not be relied upon to much better than  $0.1^{\circ}$ . It has been observed that there is an increase of the fundamental interval accompanying each rise of the ice point. The ratio of these two changes determined from the mean of all the observations taken on the 11 Jena glass thermometers is 0.035, or the fundamental interval increases by thirty-five thousandths (about one-thirtieth) of the change in the position of the ice point. This conclusion is in accordance with previous observations. The variation of the fundamental interval is of importance in the case of thermometers which show large changes of the ice point. Take, for example, a thermometer which shows a change of the ice point amounting to, say,

6°. The change in the fundamental interval will be about 0°2. Since this is the additional correction to be applied at 100° and must be added again for each 100°, the correction at 450° will amount to 0°9 (if the ice point reading is +6°, the reading at 450° will be 456°9), a quantity which can by no means be neglected. It is therefore necessary to determine this correction whenever the ice point has shown a serious change. The method of slow cooling described above renders both the ice point and particularly the fundamental interval more stable, as previously mentioned.

(h) The use of some softer glass for the stems of thermometers in connection with bulbs of Jena 16<sup>m</sup> glass is common in this country. To determine whether this practice introduces any important uncertainties in the use of such thermometers some of the experimental instruments were made up with stems of softer glass, as previously described. As changes of the ice point are due only to changes which take place in the volume of the bulb this practice could affect only the variations in fundamental interval or in calibration corrections. The latter changes are too small to be determined, and so far as can be observed with the experimental thermometers divided only to half degrees there is no difference between the changes of fundamental interval in the two cases. There is, however, a decided disadvantage in the use of the softer glass at very high temperatures. Above about 420° the glass of the stem becomes soft enough to bend. Whether this bending is due to the weight of the stem or to unequal contraction has not been definitely determined. Below 420° stems of the softer glass may be used with the advantage of being less liable to crack from sudden changes of temperature.

(i) The effect of internal pressure on the rise of the ice point is shown by comparison of curves for (Series I) thermometers G. 4279 and G. 4292, or the curves for G. 4281 and G. 4291; 4279 and 4281 being filled free from pressure and having large bulbs at the top to contain the mercury during the process of annealing. These results indicate that if the annealing temperature is lower than about 390° no difference is noticeable between the thermometers filled under pressure and those free from air. If the annealing temperature be raised to 410° or higher, the equality no longer holds true, but the thermometers filled under pressure read consistently lower. This may be due to the fact that the glass is actually softened to such an



extent that the internal pressure can have a slight effect in enlarging the bulb. According to Schott, Jena 16<sup>III</sup> glass begins to show softening at about this point.

The results here obtained would indicate that in the case of Jena 16<sup>III</sup> glass there should be a small depression of the ice point if a thermometer previously annealed free from pressure should be filled under pressure and further annealed. No data are at hand to show whether a depression actually would take place. At all temperatures between 400° and 450° this glass is apparently in a condition which is plastic as regards forces such as the internal stresses of the glass, but which is in no sense plastic as regards forces such as internal pressure. The internal strains practically disappear at these temperatures, while internal pressure produces no continuous effect which indicates plasticity, as it does, for instance, in the case of the Jena 59<sup>III</sup> glass thermometers, which showed a continuous increase in the volume of the bulb as long as they were kept at a temperature of 520° or more. Whatever the effect of internal pressure may be in thermometers of Jena 16<sup>III</sup> glass below 450° it is not large, and the observations indicate that it is possible to get good results by annealing a thermometer completely before it is filled with mercury. The subsequent changes will not cause serious trouble.

Two of the experimental thermometers were opened after the tests in such a way as to determine their internal pressure at different points of the scale. Table VII gives the results.

From this table it appears that the pressure in G. 4290 was insufficient to prevent boiling of the mercury at 450° as had been found. The vapor pressure of mercury is a trifle over 2 atmospheres at 400° and a trifle under 4.5 atmospheres at 450°.

In addition to the data given above, some results have been obtained through the kindness of Mr. L. Baudin of Paris, and the Taylor Brothers Company of Rochester, N. Y. In two letters Mr. Baudin reports the change of ice point which took place during his annealing of a total of twelve thermometers made for the Bureau of Standards from French hard glass (*Verre dur*). These thermometers are in four sets and the annealing temperature was about 445° or the temperature of sulphur vapor. The first four were heated for 72 hours showing a rise of the ice point of from 20°0 to 20°7, the next two were heated for 144 hours with a rise of 22°2 and 22°7,

TABLE VII.

*Internal Pressure in Two of the Experimental Thermometers.*

Thermometer G. 4290		Thermometer T. 55337	
Point on Scale	Pressure in Atmospheres	Point on Scale	Pressure in Atmospheres
200°C	1.1	200°C	4.2
300°	1.3	300°	5.4
400°	1.6	400°	7.7
470°	1.9	500°	13
		550°	21

the next four for 72 hours with a rise of from 18°:1 to 19°:5 and the last two for 144 hours with a rise of 21°:5 and 22°:0. These results show a considerably smaller annealing effect than found for Jena 16<sup>III</sup> glass in the present series of experiments. The Taylor Brothers Company report that six 59<sup>III</sup> glass thermometers similar to the ones used in the present tests showed a rise of ice point amounting to 59° F. (or 33° C) after heating for a total of 72 hours in 6-hour periods at a temperature of about 950° F. (510° C).

Owing to the fact that the Jena 59<sup>III</sup> glass thermometers showed an enlargement of the bulb at temperatures somewhat lower than was expected, a careful analysis of the glass from one of them was made by Mr. J. R. Cain, of the chemical division of the Bureau of Standards, with the following results. For the sake of comparison the values found by Schott & Genossen for 59<sup>III</sup> glass are given in another column.

The presence of a smaller percentage of B<sub>2</sub>O<sub>3</sub> in the present sample may account for its lower softening temperature, and the presence of both Na<sub>2</sub>O and K<sub>2</sub>O would indicate that the depression constant is larger in the present case, but this could not be determined with thermometers graduated only in single degrees. The American manufacturers of these thermometers have given us their assurance that the glass used was sent to them direct from the firm of Schott & Genossen as borosilicate glass. Thus the above analysis is probably representative of the product which can be obtained by American makers.

TABLE VIII.

*Chemical Analysis of Samples of Jena 59<sup>III</sup> Glass.*

	B. S. (Cain)	S. & G.
SiO <sub>2</sub>	72.30 per cent	71.95 per cent
Al <sub>2</sub> O <sub>3</sub>	6.14 " "	5.00 " "
Na <sub>2</sub> O	9.51 " "	11.00 " "
K <sub>2</sub> O	1.32 " "	
B <sub>2</sub> O <sub>3</sub>	10.10 " "	12.00 " "
Mn <sub>2</sub> O <sub>3</sub>	0.03 " "	.05 " "
	99.40	100.00 " "

## 7. Important Precautions.

In the foregoing pages, questions suggested have been discussed and conclusions have been drawn from the results of the present investigation. It is, however, deemed worth while to summarize briefly here the points of more immediate and practical importance.

(1) *Jena 59<sup>III</sup> borosilicate is the best thermometric glass in use, particularly for high temperatures, but it can not safely be used at much above 500°, when its composition is that of the above sample.*

(2) *Jena 16<sup>III</sup> glass can be used up to 450° or somewhat higher with good results and for temperatures lower than 420° a softer glass may be used for the thermometer stem.*

(3) *Every thermometer, particularly if intended for use above 100°, should undergo a suitable system of annealing or artificial aging before it is used. The annealing can be done before the thermometer is filled. Thorough annealing requires from four to ten days at about 450°, according to the temperature at which the thermometer is to be used, and the annealing may well be followed by a period of slow cooling for from three to six days. (The latter is, however, less important.) The total change of the ice point for this process of annealing will be about 30° for Jena 16<sup>III</sup> glass and from 20° to 30° for Jena 59<sup>III</sup> glass.*

(4) *The ice point of a thermometer will change with use at higher temperatures and must be determined occasionally if accurate results are to be had. If the thermometer has not been annealed at tem-*

peratures above  $400^{\circ}$  for 16<sup>III</sup> glass or  $430^{\circ}$  for 59<sup>III</sup>, the changes will be large if it is heated above the temperature at which it has been annealed. If changes have taken place in the ice-point reading, the fundamental interval has probably changed by about 3 per cent of this amount and the resulting error at  $500^{\circ}$  may be as much as one-fifth of the change of the ice point. [See (g) section 6.]

(5) To prevent boiling of the mercury in a thermometer the space above it should be filled with some dry, inert gas, such as nitrogen or carbon dioxide, having a pressure of one atmosphere at  $300^{\circ}$ , of four and one-half atmospheres at  $450^{\circ}$ , and of twenty atmospheres at  $550^{\circ}$ .

(6) Care must be exercised that a thermometer is not overheated. If a long portion of the stem is cold the stem correction may amount to  $30^{\circ}$  or  $40^{\circ}$ , and in this case the reading might be  $500^{\circ}$  when the temperature of the bulb was  $540^{\circ}$  and after a few minutes at that temperature the ice point might be  $20^{\circ}$  too low.

## 8. SUGGESTIONS.

The annealing oven, represented in Fig. 2, could be readily enlarged and adapted for use for annealing a large number of thermometers at a time. With the present small oven used on the ordinary incandescent lighting circuit the cost of annealing thermometers for six days and cooling for three days slowly should not exceed 50 cents each. This is a small expense since it represents the difference between a reliable instrument which will remain nearly constant and one which will show a change of several degrees after each heating. With a larger oven the cost for each instrument could be cut down at least half of the amount mentioned. Fig. 8 represents diagrammatically a regulating rheostat which could be operated automatically by means of a clock, or by hand, for gradually cooling off the oven. It is intended that the resistance of the coil between each pair of sections shall be so adjusted, by observing the resistance necessary to maintain, say, three given temperatures, that when the contact arm is set on any given section the temperature of the oven will remain at the point indicated by the number on that section. The slow cooling is not of great importance for thermometers which are not intended to be read closer than one degree or so, but a regulating rheostat would still be useful in set-

ting the temperature to the point desired. A similar oven could be designed for heating with gas and the cost might be slightly less than for an electrically heated oven, but the ease and certainty with which electric heating may be regulated and its constancy make it far more satisfactory.

Since one of the great advantages of mercurial thermometers is the direct reading scale, it is important that the corrections should be made as small as practicable. For this purpose the variations of the temperature scale defined by the different kinds of glass from

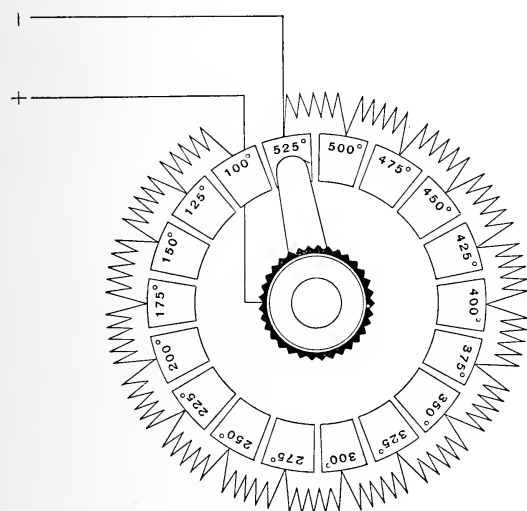


Fig. 8.—Regulating Rheostat.

the standard gas scale can advantageously be allowed for by the maker. These differences are given for two kinds of glass, Jena 59<sup>III</sup> and Jena 16<sup>III</sup>, in Tables I and II of this paper. One method of making a thermometer scale which shall read very nearly gas scale temperatures at all points is as follows: Divide the stem throughout its entire length by means of an auxiliary scale into divisions corresponding

to one one-hundredth of the volume of the fundamental interval. Then if the thermometer be of Jena 59<sup>III</sup> glass, for instance, the point 527.8 on the auxiliary scale is to be marked 500° on the thermometer; the point 469.1 is to be marked 450°, and so on, according to the table for this kind of glass. If each of these intervals be divided into 50 equal parts, the greatest error on the scale due to this method of adjusting will be only 0°5. If the points were taken every 25°, the error would be much smaller.

If it is desired that thermometers should read true temperatures when immersed to a given point, with the emergent stem at a tem-

perature different from that of the bulb, the amount of this stem correction may be computed approximately by means of the following formula:

$$\text{Stem correction} = 0.00016 \times n \times (T - t) \text{ C}^\circ.$$

$$\text{Stem correction} = 0.000088 \times n \times (T - t) \text{ F}^\circ.$$

Where  $n$  = number of degrees emergent from the bath;

$T$  = temperature of the bath;

$t$  = mean temperature of the emergent stem.

The mean temperature,  $t$ , of the emergent column may be approximately measured by means of a small auxiliary thermometer suspended near it, or for lower temperatures by surrounding the stem with a small water jacket, and taking the temperature of the water with the auxiliary thermometer, or, more accurately, in the way suggested by Guillaume, who exposes a capillary mercury thread beside the stem and thus measures its mean temperature by the expansion of the mercury thread. This is even more conveniently carried out by the Faden thermometer of Mahlke,<sup>14</sup> in which the expansion of the mercury in the long capillary (bulb) is measured by means of a still finer capillary stem. The corrections thus obtained can be combined with Tables I or II and a thermometer made to read nearly true gas scale temperatures under a given condition of immersion. For example, if the stem of a Jena 59<sup>III</sup> glass thermometer be immersed to the 100° mark, at 400° the correction due to the emergent stem (assuming 50° for its mean temperature) will be  $300 \times 350 \times .00016$  or 16.8. At 400°, according to Table I, this thermometer if divided into degrees of equal volume would read 412.3, but owing to the cooler stem it will read lower than this by 16.8 gas-scale degrees or 18.6 on the glass scale.<sup>15</sup> The reading at 400° would therefore be 393.7 and this point is to be marked 400°. Other points can be determined in the same way.

<sup>14</sup> Mahlke, *Zs. für Instrumentenkunde*, **13**, p. 58; 1893.

<sup>15</sup> The stem correction computed in this way is expressed in gas-scale degrees and should strictly be reduced to degrees on the glass scale before using it, as above. In the present example the interval 350° to 450° on the gas scale comprises 469.1–358.1 or 111 glass-scale degrees, hence one gas-scale degree equals 1.11 glass-scale degrees and 16.8 on the gas scale equals 18.6 on the glass scale. The errors of an assumed stem correction are so large, however, that reducing to glass-scale degrees might often be omitted.

Thermometers after repeated heating and cooling even at moderate temperatures as in ordinary use show a decided depression of the ice point not corresponding to any of the effects discussed above. No reliable data have yet been obtained on this point, but it is hoped that an investigation may be made and an explanation found for this apparently anomolous change in glass.

In conclusion the author wishes to acknowledge his obligation to Dr. C. W. Waidner, who proposed the present investigation, and to Dr. G. K. Burgess, both of whom have made many valuable suggestions, and to Mr. J. R. Cain, of the chemical division, for a careful analysis of glass from one of the experimental thermometers.







